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THE EFFECT OF SOLID PHASE REACTIONS ON THE BALLISTIC PROPERTIES OF PROPELLANTS

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ABSTRACT

The decomposition of NH_4ClO_4, NH_4ClO_4 containing $KClO_3$, and NH_4ClO_4-transition metal chelate mixtures has been studied under both isothermal and nonisothermal conditions (in the latter case pressure, up to 1000 psi, was an additional variable). The experimental approach was essentially a chemical one and the NH_4ClO_4 decomposition was both accelerated and decelerated by additives and environmental conditions. These results were used in helping to determine the role of the condensed phase in the overall combustion of a composite NH_4ClO_4 - fuel mixture. A mechanism is suggested for the decomposition of both catalyzed and uncatalyzed NH_4ClO_4 during the combustion of a composite NH_4ClO_4 propellant.

SUMMARY

An investigation into the mechanism of ammonium perchlorate decomposition as related to the combustion process in a composite propellant has led to the conclusion that condensed phase (including surface) reactions are important in determining the rate of the overall combustion process. Of the three possible paths by which NH_4ClO_4 can decompose only two, high temperature and sublimation, are important in the combustion process of a composite propellant over the pressure range from 300 - 3000 psi. The low temperature decomposition, even when catalyzed by the inclusion of $KClO_3$ into the NH_4ClO_4 lattice, does not accelerate the combustion process over the pressure range studied. The high temperature decomposition involves either the homogeneous (at high heat flux) or heterogeneous (in presence of catalysts) decomposition of perchloric acid. Of the additives studied the most effective catalysts are transition metals having two stable oxidation states which involve a one electron change. Generally transition metals in the form of a chelate are more effective than the same amount of metal in the form of an oxide. In addition to catalyzing, it appears to be possible to slow down the combustion rate of an NH_4ClO_4 composite propellant at low pressure by means of ammonia releasing compounds and at high pressures by basic substances which form relatively stable salts with $HClO_4$. The effect of pressure on uncatalyzed NH_4ClO_4 decomposition is to lower the deflagration temperature from $\sim 450°C$ at 15 psi to $\sim 320°C$ at 500 psi. An additional increase in pressure to 1000 psi has little further effect on the deflagration temperature.

INTRODUCTION

This program was undertaken to investigate the reactions and mechanisms of decomposition which occur in the substrate at or below the burning surface of perchlorate-containing propellants in order to determine their contribution to the overall processes which are involved in the deflagration and combustion of solid propellants. The work was carried along two parallel but interdependent paths; (1) to determine which solid phase reactions contribute to the rate of the overall combustion process, and (2) to determine mechanisms of those reactions which affect the rate of the combustion process. The primary emphasis has been on studying the change in properties of the oxidizer, ammonium perchlorate (AP), on the addition of small amounts of additives either in the AP lattice or mixed in heterogeneously. The binder (fuel) has been held constant as have such variables as particle size.

The exothermic decomposition of ammonium perchlorate most probably influences the combustion behavior of AP composite propellants. Previous studies(1-8) have revealed the principal features of the decomposition of pure AP, however there are differences of opinion on the mechanisms by which this decompositon proceeds(9). In addition, there have been studies(13-17) on the effect of catalysts, primarily transition metal oxides and salts, on the decomposition of AP with the effect of the catalysts being attributed to an increase in the rate of electron transfer at points of contact with the AP particle. This conclusion is plausible but speculative.

The first part of the program was directed at a better understanding of the mechanism of both catalyzed and uncatalyzed ammonium perchlorate decomposition. The experimental approach was to try and influence, by chemical means, the various postulated reaction mechanisms. This was done not only by introducing heterogeneous additives but by inclusion of impurities in the crystal lattice and by changing the chemical environment of the material during decomposition. The heterogeneous additives were restricted to four transition metals -- copper, iron, manganese, and cobalt. These metals were used in the form of organo-metallics or chelates. This introduced flexibility in such chemical areas as bonding of the metal and in physical areas such as solubility.

The second part of the program was aimed at relating, positively or negatively, the various mechanisms by which AP decomposes to the combustion process in an AP composite combustion system. Relatively little experimental work has been done in determining the contribution, if any, of the condensed phase decomposition to the overall combustion mechanism. The experiments in this area were designed to relate the effects (if any) of the three AP decomposition mechanisms, (1) low temperature, (2) high temperature, and (3) sublimation to the combustion process. Variables such as particle size and fuel were kept constant, however, pressure was a variable the effect of which was investigated.

When necessary, additives were synthesized to meet the demands of the program. The experimental work utilized several different thermogravimetric balances and differential thermal equipment. In addition, a pressure vessel was constructed so that differential thermal analysis could be run at pressures up to 1000 psi.

PROCEDURES, RESULTS AND DISCUSSION

I. EXPERIMENTAL

A. EQUIPMENT

All ambient pressure differential thermal analyses (DTA) were performed with a commercial instrument (duPont 900). An attachment also allowed isothermal differential thermal analysis. Pressure DTA work used the controls and recording section of the above instrument in addition to a remote cable which carried the electrical leads to a pressure vessel (Figure 1). Heating rates with the pressure equipment, due to heat losses to the pressurized atmosphere, have been limited to approximately 15°C/min. at 1000 psi. Further improvements are currently being made in this equipment.

Thermogravimetric work was performed on three different instruments. For corrosive gas atmospheres, an apparatus was used which consisted of a quartz spring in an oven heated tube and measurements were made with a cathometer. Isothermal measurements under air or nitrogen atmospheres were made with a commerical automatic recording thermogravimetric balance (Ainsworth). Non-isothermal measurements were made with an attachment to the DTA (duPont 950).

Model combustion systems were mixed with a 50 gm (Atlantic Research) horizontal mixer. The mixes were cast into straws and burned, uncured, in a Crawford bomb. Each sample was wired so as to give two separate time intervals per strand (each over a 2-inch distance).

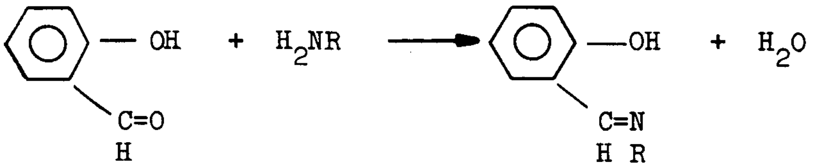
B. MATERIALS

All inorganic oxidizers were recrystallized from a water solution. Ammonium perchlorate (AP) was recrystallized until the exotherm at ~ 320°C was reduced to a minimum. The AP containing ClO_3^- ion was made by the method of Petricciari(10) starting with recrystallized AP. Organic binder materials

I, B, Materials (cont.)

were used as received. Metal chelates were generally prepared by mixing an excess of the ligand with the metal under basic conditions in water or water-alcohol solutions. In the ethanolamine series, the compounds of interest were made under neutral conditions.

In order to have metal chelates that were soluble in the organic binder, it was necessary to modify the basic ligands generally by the addition of long alkyl chains. With the Schiff bases, this is done by condensing an aldehyde (in this study salicylaldehyde) with the proper amine



A more complex procedure (with much poorer yields) was necessary to substitute alkyl chains on the methylene carbon of 2,4 pentanedione (acetylacetonate or AA). The method used involved the free radical reaction of 2,4 pentanedione, octene-1 and di-t-butyl peroxide$^{(11)}$.

C. PROPELLANT FORMULATION

The basic formulation used was

Ammonium perchlorate		75%
< 14μ	30%	
105 - 177μ	35%	
297 - 417μ	35%	
Unsaturated hydroxy (or carboxy) binder		24.64%
Metal		0.36%

I, C, Propellant Formulation (cont.)

The amount of organic ligand in the chelate was subtracted from the binder so that both metal content and total organic material remained constant.

II. RESULTS

Except for a few preliminary experiments, the emphasis in this work has been on the change in thermal decomposition properties of the oxidizer on exposure to different environments or in combination with small amounts of inorganic additives. Work was done on oxidizers other than AP primarily to shed light on the AP decomposition mechanism. AP decomposition has generally been described as occurring by three separate paths(1) and this program has attempted to evaluate the relative contributions of these three paths to the combustion process.

A. LOW TEMPERATURE DECOMPOSITION

This is the predominant decomposition path which occurs between 200 and 300°C and which stops after ~ 30% of the sample has been consumed. At the lower end of this temperature range (where there is no complication from the high temperature form), the rate and activation energy is little affected by metallic additives(9). The low temperature decomposition is sensitive to small amounts of ClO_3^- ions trapped in the AP lattice and is affected by changes in the environmental atmosphere.

1. Ammonia (NH_3) Atmosphere

If AP has been exposed to NH_3 or recrystallized from an ammonia solution, the induction period (τ) before decomposition is increased but the subsequent decomposition is not affected(1). Markowitz(12) reported that at 240°C decomposition could effectively be prevented in an ammonia atmosphere. During this study the variables investigated were: (1) percent of NH_3 in the atmosphere; (2) the point during the decomposition when NH_3 was introduced; and (3) the temperature range over which the experiments were performed. A low heating rate DTA of AP under an ammonia atmosphere showed no decomposition until the temperature was above 400°C. Under isothermal conditions, an ammonia atmosphere would prevent decomposition at any temperature up to ~ 400°C. At 400°C when nitrogen is re-introduced, decomposition begins, after a delay, in a decelerating curve similar to a sample not exposed to NH_3. Studies at 265°C (Figure 2) show that not only could decomposition be prevented, it could be stopped in either the accelerating or decelerating part of the decomposition in atmospheres 10% or greater in ammonia. Under a 5% ammonia atmosphere, decomposition appears to continue normally although there is a sharper leveling off at 30% decomposition (possibly due to decreased sublimation). After decomposition ceases and ammonia is replaced by nitrogen, there is a relatively long delay before decomposition resumes. Although there is a small increase in acid concentration in AP that has been decomposed to 30%, a brief exposure of this material to ammonia does not result in any further decomposition. This would argue against decomposition ceasing at 30% due to a build-up of perchloric acid.

2. Hydrogen Chloride (HCl) and Chlorine (Cl_2)

Both of these gases modified the shape of the decomposition curve from what it is under a nitrogen atmosphere. One interesting point is that neither gas affected the induction period at a given temperature. Once decomposition started, both HCl and Cl_2 accelerated the 30% decomposition; however, HCl had little effect beyond this point while Cl_2 caused the decomposition to go to completion in a continually decelerating curve.

II, A, Low Temperature Decomposition (cont.)

3. Effect of ClO_3^- on AP Decomposition

The effect of ClO_3^- on AP decomposition has previously been investigated by DTA(10). It was noted that there is an exothermic reaction after the AP phase transition whose position and magnitude is a function of the ClO_3^- concentration. However, at no concentration does the exotherm occur before the AP phase transition. Thermogravimetric work has now shown that the ClO_3^- ion accelerates the low temperature (30%) decomposition of AP. Once this phase of the decomposition is over, the remaining AP decomposes at the normal uncatalyzed rate, Figure 3. While the low temperature decomposition of pure AP always levels off at approximately 30% of total decomposition, the percent attainment of total decomposition is a function of temperature when ClO_3^- ion is incorporated into the AP crystal. With increasing temperature, in isothermal decompositions, the percent of total decomposition decreases up to the AP phase transition and then increases slightly. The shape of the curve remains sigmoid with the percent of total decomposition ranging from ~ 60% at 200°C to ~ 24% at 240°C. The chlorate ion reduces but does not eliminate the induction period. Table 1 lists some representative times for the accelerated decomposition and the percentage of total decomposition as a function of temperature. Due to the exothermic nature of the decomposition above 240°C (however not below 240°C as determined by isothermal DTA) it was not possible to treat the decomposition kinetically. It was, however, possible to do this using the induction time as a measure of the rate. A plot of log τ against 1/T°K for AP containing 0.035% ClO_3^- and for 0.07% ClO_3^- gave activation energies of 24.8

II, A, Low Temperature Decomposition (cont.)

± 2 Kcal/mole and 26.1 ± 2 Kcal/mole, respectively. If the ClO_3^- containing material is decomposed under an ammonia atmosphere, it behaves as pure AP under similar conditions. The large broad exotherm at 300 - 325°C is shifted to a sharp exotherm at ~ 400°C and weight loss is prevented until this higher temperature (Figure 4).

For burning rate studies, AP containing 0.1% $KClO_3$ was screened into various particle sizes. This oxidizer was then used to obtain burning rates with the standard combustion model formulation. The burning rate data showed that there was no increase in burning rate over the pressure range of 300 - 2500 psi. In fact, there was a decrease at higher pressures but this has not yet been reconfirmed.

TABLE 1

ISOTHERMAL DECOMPOSITION OF AP CONTAINING 0.07% $KClO_3$

Temperature °C	Induction Time (τ) min.	% Decomposition	Fast Portion of Decomposition %	Fast Portion of Decomposition Time (min.)
290	2.75	32	26	3.7
280	3.33	32	21	7.0
270	4.50	33	28	15
259	7.50	31	21	18
239	23.5	24	15	52
230	49.0	27	17	106
220	51.0	26	17	105
210	90.0	37	30	186
200	179.0	60	43	349

II, Results (cont.)

B. HIGH TEMPERATURE DECOMPOSITION

Most metallic additives affect the high temperature decomposition of AP. In the uncatalyzed case, this decomposition does not become appreciable until ~ 400°C; however, in the presence of catalysts, rapid decomposition rates may occur as low as 260°C (just above the AP phase transition).

Most of the previous work on catalysis has been done with transition metal oxides(13-17). The approach in this work was to use a series of transition metal chelates as additives. This was to permit variations in bonding of the metal and to compare various metals under the most controlled conditions (bonding, solubility in binder, etc.). The metals selected were Cu, Fe, Mn and Co. Isothermal kinetic studies using these materials turned out to be impossible as they all interacted with the AP, many of the reactions being exothermic. Even if the material was stable up to the time of reaction, the products of decomposition reacted so that the overall reaction altered the additive. However, this did not prevent some interesting and useful data from being obtained with these systems.

Before looking at the catalyzed system, AP was investigated thermogravimetrically under transient heating conditions. It was found that the AP decomposition changed from a controlled to a run-away reaction whenever the sample temperature reached 475°C. Under heating rates of 10°C/min., almost 90% weight loss occurred before this temperature while at 50°C/min., only about 20% prior decomposition occurred. In the catalyzed system this temperature was lowered to between 260 - 360°C and generally was preceded by little or no loss of weight.

II, B, High Temperature Decomposition (cont.)

Since copper in almost any compound showed reasonable activity in the decomposition of AP, it was chosen for most of the early work. One of the most versatile series of chelates were the salicylaldehydeimine Schiff bases. The coordinated bonding in these compounds is through the oxygen and nitrogen atoms of the ligand. Table 2 lists properties of some representative compounds. In addition, several chelates are listed in which at least one of the bonding atoms was part of a ring structure. It can be seen that these latter compounds are generally more stable thermally although the thermal stability of the salicylaldehydeimine can be increased when the two ligands are connected with a bridge such as ethylene diimine. The large range in solubility can also be seen as a function of the alkyl chain. When a series, which varied only in solubility, of these Cu compounds was incorporated into a propellant (constant Cu content), their burning rates were identical below ~ 1000 psi. Above this pressure, the more insoluble materials resulted in a leveling off of the pressure slope (Figure 5). Subsequent work showed this type of pressure exponent resulted when the ligand was used without the metal.

Another series of chelates was made using ethanolamines as ligands. These compounds underwent an internal redox reaction at their melting point(18) and then interacted exothermically with AP below the phase transition. The product of this internal redox reaction, which was the active compound, was never really identified except that it appeared more polymeric than crystalline. Propellant burning rates with these materials resulted in considerable acceleration at pressures below 1000 psi, but also leveled off above this pressure.

II, B, High Temperature Decomposition (cont.)

Work was extended to more fully identify the reaction and products that occur when organo-metallics interact with AP at low temperatures. The low temperature exothermic interaction between AP and copper triethanolamine is non-reversible (Figure 6) as in the similar case of ferrocene. However,

TABLE 2

THERMAL AND SOLUBILITY PROPERTIES OF SOME COPPER (II) CHELATES

Ligands	Solubility (mg/cc hexane)	Melting Point, °C
N-substituted bis-(salicylaldehydeimine) Cu(II)		
R = methyl	0.32	160 [a]
ethylene	I	320
butyl (C_4)	14.0	80
octyl (C_8)	446	~50
dodecyl (C_{12})	611	~60
octadecyl (C_{18})	29.6	~60
Triethanolamine	I	135
Salicylaldehyde	I	260
8-hydroxyquinoline	I	325 [b]
Acetylacetonate	I	280
Phthalocyanine	I	>400 [b]

I = insoluble (<0.05 mg/cc)

[a] melts reversibly

[b] stable with AP up to 240°C

even with those additives where there is no thermal indication of interaction there is chemical evidence for a reaction. In order to determine what these interactions between the oxidizer and additive are, $Cu(AA)_2$ was added to $KClO_4$ and NH_4Br. $Cu(AA)_2$ was selected as it was stable in air up to its melting point but reacted with AP prior to this point. A DTA trace shows that in the presence of $KClO_4$ the $Cu(AA)_2$ melts (~280°C) as in air and with no indication of an interaction with the $KClO_4$ below ~ 340°C. The trace with NH_4Br shows that by 300°C the $Cu(AA)_2$ has interacted with the NH_4Br, and chemical evidence indicated this interaction occurred below 200°C.

The exothermic interaction of AP with ferrocene at 180°C results in a product of indefinite composition which X-ray analysis and IR do not help to identify. An approximate analysis is Fe 11.5%, N 7.1%, O 20.2%, C 51.8%, and H 3.2%. The material is insoluble in hot alkali or hot acid but decomposes to Fe_2O_3 in air (but not nitrogen) at temperatures above 400°C. The material is finely divided and generally ignites when heated in air. This product does not exothermically interact with AP as does ferrocene (Figure 7). Figure 8 shows the difference in burning rates with the two materials at constant iron content. This type of low temperature interaction was also obtained when ruthenium was substituted for iron, e.g., $Ru(cp)_2$.

When acetylacetonate (AA) was mixed in a propellant, it resulted in no change in the control burning rate; therefore, this ligand was selected for a series of chelate additives. Most of these compounds melt (Table 3) at or below the phase transition temperature of AP and result in AP decomposing

II, B, High Temperature Decomposition (cont.)

exothermically near the phase transition. The iron chelate shows a low temperature interaction similar to those of $Fe(cp)_2$ and $Ru(cp)_2$ with AP. This interaction is different from the low temperature exothermic decomposition of AP caused by other metal chelates (Co, Mn, and Cu). The exothermic reaction with the iron compound, at moderate heating rates, goes to completion (peak at ~205°C) before the AP decomposition has really begun. The decomposition of AP begins after this interaction, and it appears at least qualitatively to be less exothermic than the similar decomposition in the presence of $Co(AA)_3$, $Co(AA)_2$, or $Mn(AA)_3$.

TABLE 3

2,4-PENTANEDIONE TRANSITION METAL CHELATES

Compound	Melting Point, °C	
$Fe(AA)_3$	179	
$Cu(AA)_2$	280	
$Mn(AA)_3$	165	Redox reaction and loss of one AA
$Mn(AA)_2$	260	Melts with reaction
$Co(AA)_3$	240	
$Co(AA)_2$	Sublimes	Loss of any coordinated solvent between 120 - 150°C

The $Cu(AA)_2$ and $Fe(AA)_3$ were modified to increase their solubility in the binder by putting alkyl chains (branched and straight) on the methylene carbon of the AA. DTA showed that the change in ligand did not affect the chelate's action with AP. The burning rate results indicate no essential difference between the soluble and insoluble additives over the entire pressure range. Figure 9 shows representative burning rates with different AA chelates as catalysts.

If a heterogeneous type catalyst is added to the AP and the system decomposed under an ammonia atmosphere, the results are quite different from pure AP or AP containing $KClO_3$. The temperature at which deflagration occurs remains the same under ammonia as it is under nitrogen (for copper chromite ~320°C, Figure 10). There is a greater weight loss prior to deflagration under nitrogen than under ammonia and with Cu0202 while the sample in nitrogen deflagrated, that in ammonia detonated. An attempt to isothermally decompose AP + Cu0202 under ammonia at 265°C resulted in a detonation which destroyed the quartz spring and blew out the top seal of the apparatus. At approximately this time, an SRI report(19) showed that they also found that the rate of AP decomposition catalyzed with Cu0202 was the same under nitrogen and under a partial pressure of ammonia. Detonation may result in these experiments from the increased concentration of NH_3 (possibly adsorbed on the Cu0202) with which the perchloric acid decomposition products can react.

C. EFFECT OF BASIC MATERIALS

The change in the burning rate plot when the basic salicylaldehydeimine ligand was used suggested some preliminary investigation of this phenomena. When propellants were formulated with 1% of a tertiary amine (tributyl and dimethyldodecyl), the propellant had a greatly reduced burning rate and pressure exponent, Figure 11. The effect becomes more pronounced with increasing pressures. When 10% $(NH_4)_2 SO_4$ was mixed into a propellant, there was a noticeable effect on burning rate; however, this effect was primarily at the low pressures, Figure 12. These experiments are only preliminary but shed important light on the overall combustion mechanism.

D. EFFECT OF PRESSURE

The pressure DTA made it possible to look at some of the important reactions as a function of pressure. Work with the pressure DTA indicates the greatest effect of pressure (separated from heat flux), in the range from 15 psi to 1000 psi, is at the lower pressures. Relatively large changes occur between 15 - 250 psi while little change is noted from 500 - 1000 psi. It is noted that under all pressures the first detectable exothermic decomposition occurs at ~310°C. Increasing pressure does not appreciably affect the temperature at which decomposition begins but does affect the rate of decomposition at that temperature, Figure 13. Waesche(22) does not find as large of a change in the final deflagration temperature of AP with pressure as we do; however, work at SRI(27) fairly well confirms our experiments. Experimental details are not given on the pressure containers used by Waesche in his AP decomposition experiments using differential scanning calorimetry. It is possible with the size and geometry (small sample with a large surface area in contact with the environment) of the sample used in DSC experiments that much of the heat generated in the decomposition may be effectively dissipated by the compressed gas environment (i.e., the compressed gas is a good heat sink). Additives generally lower the deflagration of AP to these lower temperatures at ambient pressure; however, pressure increases do not further lower this temperature. There appears to be a limiting temperature below which AP will not deflagrate (pure or catalyzed), at least in the pressure range studied. It is, however, possible to increase this temperature by adding basic additives (amines) for those which release NH_3 on decomposition, e.g., $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$, Figure 14.

At 500 psi there is very little difference between the DTA patterns of various additives which do not react with AP. With the additives which do react, there is a slight increase in the magnitude of the low temperature exotherm with increasing pressure.

III. DISCUSSION

A. LOW TEMPERATURE AP DECOMPOSITION

The low temperature mechanism of AP decomposition has been investigated by many workers and most generally ascribed to an electron transfer process. Recently Jacobs(9) has reexamined this work and come to the conclusion that all AP decomposition processes have the same rate determining step -- proton transfer.

The idea that the uncatalyzed decomposition of AP, over most of its temperature range, is governed by a proton transfer mechanism in which NH_3 and $HClO_4$ are formed in the rate determining step has some support from present studies of AP decomposition under an ammonia atmosphere.

The retarding effect of NH_3 on the decomposition of AP can be understood if the first step in the decomposition involves equilibrium

$$(1) \qquad NH_4ClO_4 \rightleftharpoons NH_3 + HClO_4$$

That HCl accelerates but does not basically alter the pattern of decomposition is consistent since it does not enter the rate determining equilibrium (except possibly to form some NH_4Cl which sublimes faster than NH_4ClO_4). The effect of Cl_2 may be due to its thermodynamic potential to oxidize ammonia and displace the equilibrium to the right (whether it has the kinetic reactivity, at this temperature, to do this has not yet been established). Unlike the HCl, the Cl_2 continues to affect decomposition after the intermosaic material (30%) has been consumed. Neither gas affects the induction time.

III, A, Low Temperature AP Decomposition (cont.)

Additional information on this process comes from the observations with material containing small amounts of ClO_3^- ion. The $KClO_3$ is not isomorphous with NH_4ClO_4 so that the material will be concentrated at disorganized parts of the lattice. This can be seen by the reduction (but not elimination) of the induction period and by the acceleration of decomposition being limited to the 30% decomposition (i.e., interstitial material). If $KClO_3$ is mixed heterogeneously with AP, there is no effect on AP decomposition. The ClO_3^- ion has only a small effect on the rate of AP decomposition below 240°C; however, at very low temperatures (~200°C) it increases the extent of this decomposition to 60%. Below the AP phase transition it appears as if the ClO_3^- is trapped in the essentially rigid ClO_4^- determined lattice and has only a moderate effect on the AP decomposition. As soon as the anion part of the lattice is free to rotate, there is an accelerated decomposition due to the ClO_3^- ion and the reaction becomes exothermic. If the reaction at this point was between ClO_3^- and NH_4ClO_4, there should be no effect of an ammonia atmosphere. Since NH_3 completely retards this reaction below 400°C (similar to pure AP), the ClO_3^- must react with the dissociation products (NH_3 or $HClO_4$), with products of their decomposition, or form favorable sites for these reactions. Since the exotherm due to this reaction is not eliminated but displaced to a higher temperature, the reaction of ClO_3^- is either not with NH_3 or the NH_3 from the atmosphere does not come into intimate enough contact with the ClO_3^- in the solid. The ClO_3^- could enter in a scheme similar to that of Rosser(19) and react with $HClO_4$

$$HOClO_3 + ClO_3^- \longrightarrow 2\ ClO_3 + OH^-$$

$$2\ ClO_3 \longrightarrow 2\ ClO_2 + O_2$$

(instead of Rosser"s scheme of two perchloric acid molecules reacting). Since a very small quantity of this material effects a large change in rate, it must be either catalytic (regenerate ClO_3^-), produce other reactive intermediates, or form favorable sites at which decomposition can occur.

As the temperature approaches 400°C, decomposition of AP occurs even in an ammonia atmosphere. This cannot be due only to the thermal breakdown of the ClO_4^- ion (since there are salts with freely rotating ClO_4^- ion which do not decompose at this temperature). There may be enough association of a proton with the ClO_4^- at these temperatures to initiate what becomes a "run-away" reaction from the thermal breakdown of $HClO_4$.

B. HIGH TEMPERATURE AP DECOMPOSITION

Heterogeneous catalysts such as metal oxides and transition metal chelates have little effect on the low temperature decomposition but do affect the high temperature rate. Not only do they result in an increase in the overall rate of the AP decomposition but a change in the rate determining step. The activation energy for the high temperature decomposition of uncatalyzed AP is ~30 kcal/mole(9), while for most of the catalyzed reactions it is ~45 kcal/mole(20). This latter value is close to the energy involved in the breaking of the $HO - ClO_3$(21) bond in perchloric acid. Waesche(22) measured the heat of decomposition for catalyzed and uncatalyzed AP and found a significant difference between the two paths. The Q for the uncatalyzed decomposition was ~260 cal/gm while that for a copper chromite catalyzed decomposition was ~370 cal/gm.

III, B, High Temperature AP Decomposition (cont.)

There is an increasing amount of evidence that the decomposition of AP under high heat fluxes and the catalyzed decomposition under moderate heat fluxes involves the decomposition of perchloric acid. In some interesting experiments, Saunders and Pellett(23) have shown that when AP is decomposed by a pulsed ruby laser in the presence of Fe_2O_3, MnO_2 and copper chromite the major fragments (as detected by a mass spectrometer) are NH_3, HCl, ClO_2, ClO, HOCl, NO and H_2O; $HClO_4$ is quite small in comparison to that found in the low temperature decomposition(24). In the present program it was found that in the presence of heterogeneously added metal oxides or chelate catalysts the decomposition of AP proceeds the same under ammonia and nitrogen atmospheres. Since under NH_3 the equilibrium lies almost entirely on the side of the undissociated material the catalysis appears to be in the solid phase. The activation energy that Jacobs(20) finds for the decomposition of AP + Cu0202 and that Levy(21) finds for the decomposition of $HClO_4$ are almost identical. The perchloric acid decomposition could be similar in the solid phase even if the proton is not fully transferred. At temperatures where both NH_4^+ and ClO_4^- are freely rotating it would be possible to have an intermediate, NH_3---H---$OClO_3$, whose catalyzed decomposition would be similar to $HClO_4$. The products of this decomposition can then further react with NH_4^+ (or NH_3). That the catalyzed decomposition involves $HClO_4$ and not just the ClO_4^- ion is indicated by similar experiments using $KClO_4$ as the oxidizer. When adding the same additive as in the AP experiments and passing ammonia over the sample, no detectable reaction occurred. This is true even at temperatures higher than those at which the AP deflagration occurred. At these temperatures (above 300°C), the ClO_4^- ion of the $KClO_4$ is freely rotating as it is at the deflagration temperature of AP.

Although many compounds were tested (using the four selected metals) their overall effects on the AP decomposition as followed by DTA were surprisingly similar. At ambient pressure, they all lowered the deflagration temperature to between 320 and 380°C. This temperature range became even narrower with an increase in pressure and it appears there is a lower limit to the temperature at which AP can be catalyzed to deflagration. This is most probably the temperature at which the heterogeneous decomposition of $HClO_4$ becomes appreciable. Differences in the catalysts are most likely due to the rate at which they catalyze the decomposition of AP at this temperature. Considering the rate is rapid and the maximum difference between catalysts in an AP composite propellant is $\sim$ a factor of 2, the difference would not be detected by these experiments. One qualitative observation is that in the DTA experiments copper compounds often cause detonation rather than deflagration (and generally are the most effective catalysts in propellants).

One general division that can be made between additives is that one group only catalyzes the AP decomposition while the other group not only catalyzes but exothermically interacts with the AP. This exothermic interaction is generally at temperatures below the phase transition of AP. Comparison studies with other ammonium and perchlorate salts indicate that both the ammonium ion (or similar ions such as methyl substituted ammonium ions) and the perchlorate ions are necessary for this reaction. An interaction not detectable by DTA (but detectable chemically) occurs between many of these additives and the ammonium salts but not with the perchlorate salts. This would indicate the initial step is a reaction between the metal chelate and the ammonium ion which is then followed by an interaction of one of these products and the perchlorate ion. It is this second step which results in the exothermic part of the reaction. Examples of this type of reaction are found with additives such as ferrocene and copper triethanolamine chloride.

C. COMBUSTION

The 'low temperature' decomposition of AP does not affect the burning rate of a composite propellant with normal thermal diffusivity. A comparison of the frequency factor and activation energy of the low temperature decomposition of AP and that of sublimation of AP shows them to be about equal(9). However, the values for the low temperature decomposition are for the decomposition process which occurs after the inducation time (τ). The induction time varies with temperature and a plot of τ against 1/T results in an activation energy similar to that of the decomposition process. Using this information, the value of τ can be computed

$$\left[\ell n(\tau_1/\tau_2) = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

for higher temperatures. These computations show that the value of τ at 500°C ($\sim$300 msec.) is long in comparison to processes occurring in a burning propellant. The value of τ at 500°C is longer than the time from when a point in the propellant grain first experiences a temperature rise to the time at which it deflagrates ($\sim$10 - 30 msec.). This latter time is a function of the temperature profile of the propellant and the burning rate; however, it is short compared to τ for most composite propellants.

The mechanism that becomes competitive with sublimation is the catalyzed high temperature decomposition. It is in this area that most additives affect the burning rate of a composite propellant. Most of the evidence both indirect (this work) and direct (Reference 23) indicates that this process involves the decomposition of perchloric acid.

The effectiveness of an additive in altering the burning rate of propellant varies with different metals and with different compounds of the same metal. Chelates, [bis-(N-R salicylaldehydeimine) Cu(II)], identical in all properties except solubility in the fuel, resulted in identical burning rates between 300 - 1000 psi but differed above this pressure (the soluble additive had the higher burning rate at the high pressures). Since this ligand itself has an effect on the burning rate (lowering it in a similar manner as the amines discussed below), the effect of solubility was reinvestigated with a series of acetylacetonate (AA) chelates. In a comparison of four insoluble transition metal acetylacetonate chelates (equal mole percent), the effectiveness of the metals as burning rate accelerators at pressures below 1000 psi is $Cu > Fe > Co \simeq Mn$, Figure 8. At higher pressures, this order breaks down; however, copper is the most effective metal over the entire pressure range. Soluble copper and iron chelates of this same series gave essentially the same burning rates (over the entire pressure range) as did the insoluble compounds. In the combustion situation, the effect of the catalyst in the condensed phase must be at the surface of the oxidizer. Since the insoluble compounds tested melt below the deflagration temperature of AP, it is possible that both the melted insoluble and the binder soluble chelates had comparable contact with the oxidizer in the propellant.

A generalization that can be made is that for a given amount of metal there is a greater effect if the metal is bound in some organo-metallic compound (or chelate) than if it is present as an ionic salt or oxide. The catalyst affects the proton transfer equilibrium by removing one of the products thereby driving the reaction forward. It does this by affecting the heterogeneous decomposition of perchloric acid. There are several reasons why an organo-metallic compound would be expected to be more effective than an oxide in this reaction: (1) if the organo-metallic first decomposes to the oxide it would be in molecular size particles with fresh surfaces, i.e., formed in situ, and (2) if the catalyst is the original additive or a metal-organic product of an earlier interaction, a similar result would be expected as not only do metals promote $HClO_4$ decomposition, $HClO_4$ reacts exothermically with most organic substances. With an organo-metallic additive both processes could occur, with the possibility of an overall additive effect on the rate of decomposition of the $HClO_4$. The two most effective metals, copper and iron, have two stable oxidation states separated by a one electron change. On the other hand, while manganese has many oxidation states, the two most stable states (+2 and +4) are separated by two electrons. While cobalt involves only a one electron change between its two oxidation states, the +3 state is unstable due to the potential of this couple (∿ - 1.8v).

The work with the effect of bases on propellant combustion is preliminary. However, further evidence for the decomposition of $HClO_4$ being one term in the overall kinetics of combustion of an AP composite propellant comes from the stabilizing effect derived from small amounts of an added base. When propellants were formulated with 1% of a tertiary amine (tributyl and dimethyl dodecyl), the resultant propellant had a greatly reduced burning rate and pressure exponent. Since there is only 1% of the basic amine for 75% AP, the effect is most likely a surface effect, possibly the neutralization of $HClO_4$. This would still allow NH_3 to desorb while both slowing the desorption of $HClO_4$ and stabilizing the $HClO_4$ on the crystal surface. The difference in slope between the soluble and insoluble copper chelates with the basic salicylaldehydeimine ligand may be explained due to the difference in availability of the base at the oxidizer surface. The basic portion of the soluble chelate was not as available (tied up in the binder) as that from the insoluble chelates and therefore had less (or no) effect on the burning rate.

The burning rate data with the propellant containing ammonium sulfate tends to corroborate some finding which showed the largest effect on the burning rate of AP propellants under an ammonia atmosphere(25) was at the lower pressures. These data suggest a change in the rate controlling mechanism with increasing heat flux (a change to a mechanism that does not require desorption of NH_3). This same change is suggested by the AP decomposition, under an ammonia atmosphere, which occurs at temperatures over 400°C. Summerfield(26) has found some similar anomalous behavior (plateaus, etc.) using small particle size AP. He postulated for a given set of conditions the anomalous behavior is accentuated with increasing spread between the fuel and the oxidizer surface temperatures. In our experiments which use a large particle size distribution, the plateau and negative slope come as a result of an increase in the decomposition temperature of the oxidizer (and, therefore, decrease the spread between fuel and oxidizer decomposition temperature).

CONCLUSIONS

1. We believe that a substantial amount of evidence has been collected which indicates that the condensed phase decomposition (including surface reactions) is at least one important term in the rate determining step over part of the pressure range for an uncatalyzed AP composite propellant and over most (if not all) of the pressure range for a catalyzed AP composite propellant.

2. The low temperature AP decomposition proceeds by a proton transfer mechanism. This decomposition, even when catalyzed by the inclusion of $KClO_3$ into the AP lattice, does not accelerate the burning rate of an AP composite propellant over the pressure range of 300-3000 psi.

3. The high temperature AP decomposition involves the decomposition of $HClO_4$. Deflagration results only when the AP is in the cubic modification (NH_4^+ and ClO_4^- ions are both freely rotating). This $HClO_4$ decomposition becomes appreciable in the presence of additives (heterogeneous) above ∿250°C and without additive (homogeneous) above ∿400°C.

4. The rate determining step remains the same for all heterogeneously added transition metal catalysts. They differ only in the rate at which they catalyze the reaction.

5. Generally organo-metallics are more effective catalysts than metallic oxides or salts. Metals having two stable oxidation states separated by one electron appear to be the most effective catalysts. In the series of metals studied the catalytic effectiveness is as follows $Cu > Fe > Co \sim Mn$.

Conclusions (cont.)

6. There is no difference in catalytic effectiveness between a chelate which is soluble in the binder and one which melts below the temperature (∿320°C) at at which AP deflagrates during combustion.

7. The effect of the heat released by a low temperature AP-additive reaction is to increase the burning rate. This effect is greatest at low pressures (low heat fluxes).

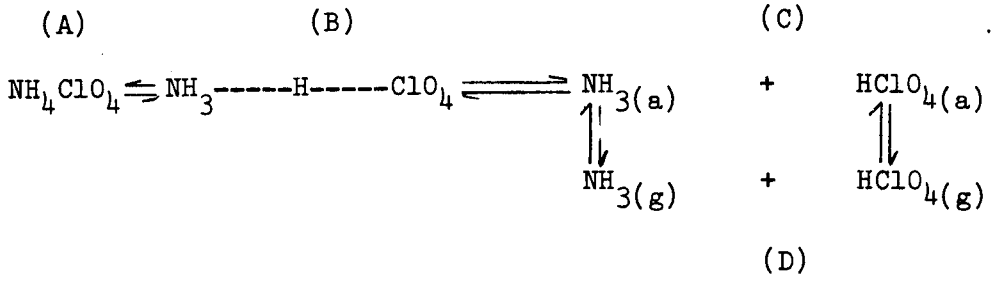
8. The retarding effect of free NH_3 on combustion is greatest at low pressures while the retarding effect of added bases is greatest at higher pressures.

9. The effect of pressure is to reduce the deflagration temperature of uncatalyzed AP from ∿450°C to ∿310°C. This is approximately the deflagration temperature of catalyzed AP at ambient pressure. The temperature of the catalyzed system does not appreciably decrease with increasing pressure.

10. In an AP composite propellant the high temperature decomposition mechanism and sublimation are competitive paths for the AP decomposition. Their relative contributions are a function of pressure, heat flux and catalyst. The relative contribution from the high temperature decomposition increases with pressure and in the presence of catalysts.

11. A mechanism is offered for correlating existing data and designing future experiments.

Conclusions (cont.)



$$\begin{tikzcd}
(A) & (B) & & (C) & \\
NH_4ClO_4 \arrow[r, shift left] & NH_3\text{-----}H\text{-----}ClO_4 \arrow[l, shift left] \arrow[r, shift left] & NH_{3(a)} \arrow[l, shift left] \arrow[d, shift left] & + & HClO_{4(a)} \arrow[d, shift left] \\
& & NH_{3(g)} \arrow[u, shift left] & + & HClO_{4(g)} \arrow[u, shift left] \\
& & & (D) &
\end{tikzcd}$$

(A) AP below 240°C with a ClO_4^- ion determined lattice

(B) AP above 240°C with both ions rotating freely

(C) NH_3 and $HClO_4$ absorbed on the surface of the AP

(D) NH_3 and $HClO_4$ after desorption

Low Pressure and Moderate Heat Fluxes: Under these conditions the decomposition rate of an uncatalyzed system is most likely controlled by the sublimation (C)→(D). It is this process that is retarded by an ammonia atmosphere. If a catalyst is present, it promotes the decomposition of perchloric acid at (B) or (C) on the surface of the crystal. For these purposes, (B) and (C) are not totally distinct, that is, it is not clear at what point in the proton transfer the hydrogen ion is close enough to the perchlorate ion to result in an entity which can decompose as perchloric acid. That the decomposition involves perchloric acid and not perchlorate ion has been shown by the stability of $KClO_4$ at these temperatures in the presence of additives and an ammonia atmosphere. The catalyzed path involves the heterogeneous decomposition of perchloric acid at the surface of the AP. When bases such as amines are added, they neutralize the $HClO_4$ at the surface (C).

Conclusions (cont.)

In the uncatalyzed system, the base does not interfere with the desorption of ammonia but does slow up the desorption of the $HClO_4$ (interferes with the $HClO_4$ part of the $(C) \rightarrow (D)$ process). Although in the catalyzed system the decomposition takes place without desorption, the perchloric acid would be more strongly bound in a salt formation with the added base than with NH_3 (the added base being a stronger base than NH_3). It is expected that this salt formation would affect the combustion rate of the composite propellant.

High Heat Fluxes: At high heat fluxes, the decomposition of both the catalyzed and uncatalyzed system would be occurring at (B) or (C). The catalyzed system would again be essentially controlled by the heterogeneous decomposition of $HClO_4$, while in the uncatalyzed case there would be at least one path involving the homogeneous decomposition of $HClO_4$ at the surface. Direct evidence supporting the catalyzed path is found in the work of Saunders and Pellett(23) who found the primary decomposition products of catalyzed AP decomposed by a laser to be NH_3, HCl, ClO_2, ClO, HOCl, NO and H_2O. In the uncatalyzed system homogeneous decomposition of $HClO_4$ at the surface would account for the normal burning rates under an ammonia atmosphere at high pressures (heat flux), and the decomposition of AP under ammonia at temperatures above ∿400°C.

Those paths which involve perchloric acid decomposition at the surface might be expected to be sensitive to the type and quantity of fuel, since this path allows a possible interaction between very reactive oxidizer decomposition products and the fuel at points of intimate contact. This may

Conclusions (cont.)

account for the effect of fuel at high pressures in uncatalyzed systems[28] and the relative changes in effectiveness of catalysts on changing the binder system.

The effect of pressure (and the related heat flux) on the combustion process is noticeable in all of the preceding work. Over the pressure range of 0 - 3000 psia there appear to be three pressure regions in which different mechanisms may be rate controlling. These regions do not have sharp boundaries but are from 0 - 300 psia, 300 - 1000 psia, and above 1000 psia. This breakdown has been suggested previously by Powling[28] but not necessarily for the same reasons as those from the current program. The change at ∿1000 - 1200 psi is suggested by the work with ammonia and bases as well as by the increased effect of fuel on combustion rates in this pressure region. Therefore, in a meaningful discussion of AP propellant combustion the pressure range (and heat flux) must be specified.

More work is needed to completely define the mechanism of combustion of a composite AP-fuel system (both catalyzed and uncatalyzed) over the pressure range of 1 - 3000 psi. This will have to include a look at the variables of particle size and fuel. In attempting to tailor burning rates it is interesting to note that while considerable variations exist between additives the maximum acceleration obtained with an additive in an AP composite propellant is of the order of a factor of 2 or 2.5. If a large acceleration (factor of 4 or 5) is desired, we believe there is strong evidence that major modifications such as auxiliary oxidizers or reactive additives (in more than catalytic quantities)

Conclusions (cont.)

will be needed. A second interesting point is that it is possible to develop slow burning AP composite propellants; however, this area is too new to set even approximate limits on at this time.

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BLOCK DIAGRAM OF PRESSURE DTA

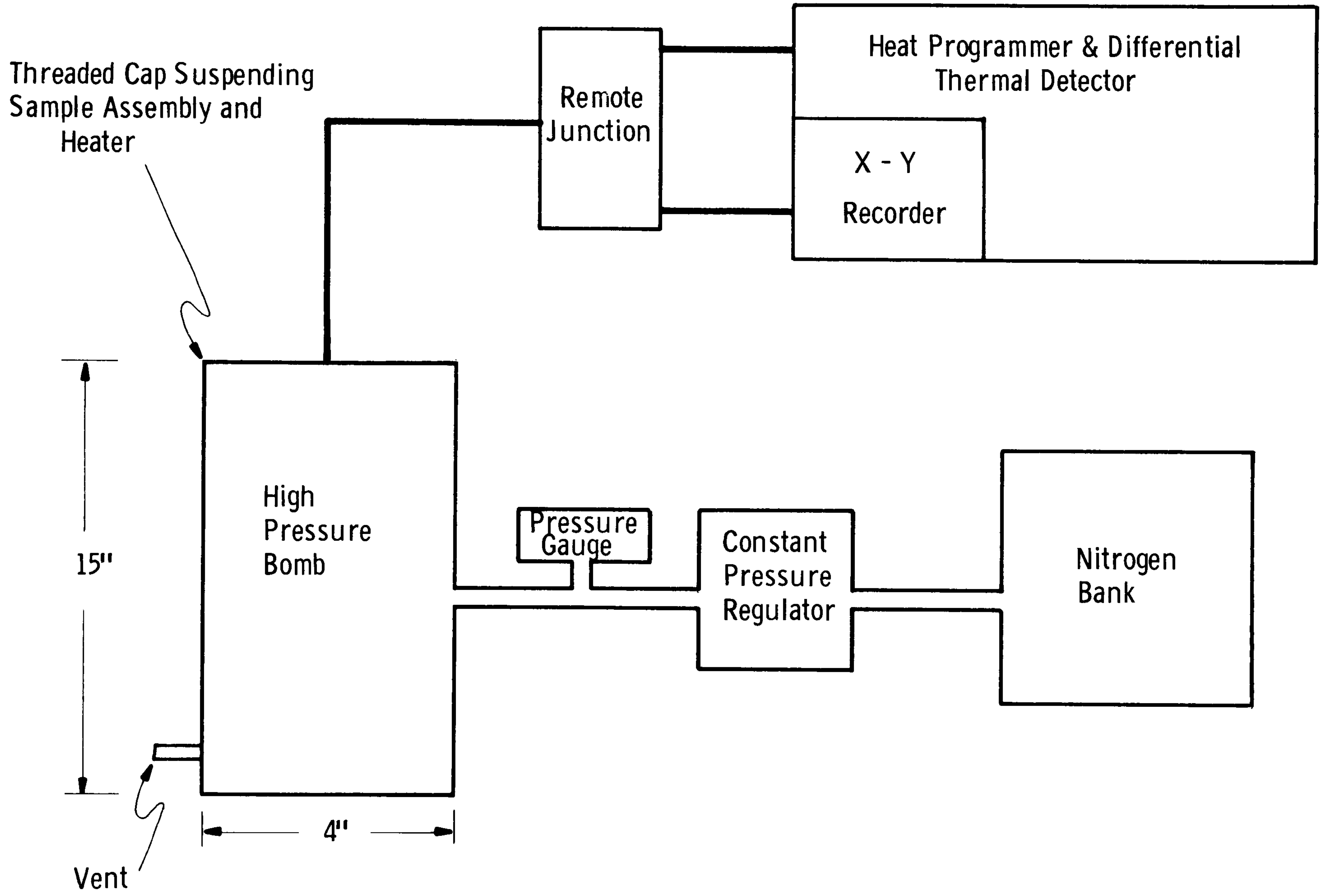


Figure 1

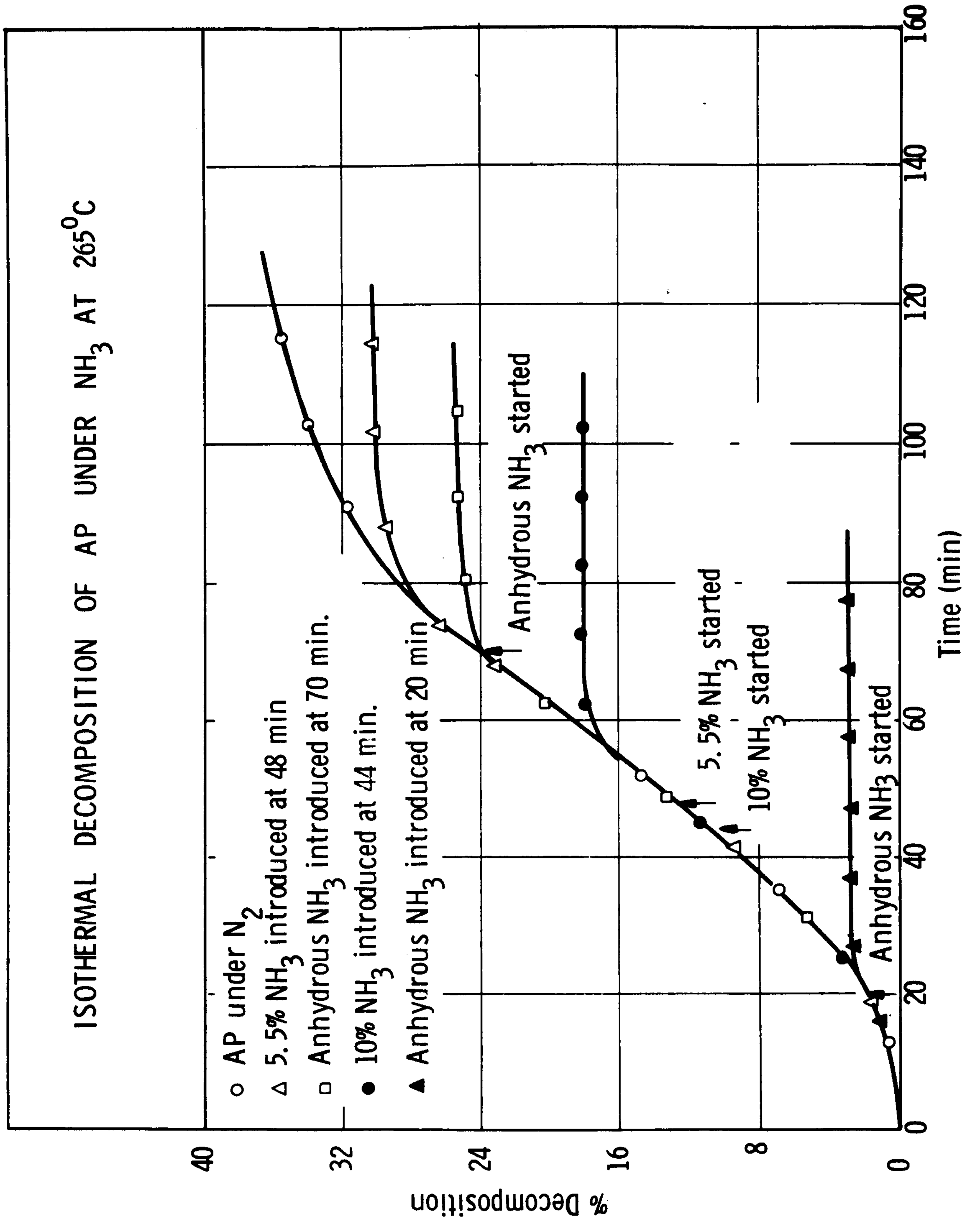

ISOTHERMAL DECOMPOSITION OF AP UNDER NH3 AT 265°C
○ AP under N2
△ 5.5% NH3 introduced at 48 min
□ Anhydrous NH3 introduced at 70 min.
● 10% NH3 introduced at 44 min.
▲ Anhydrous NH3 introduced at 20 min
Anhydrous NH3 started
5.5% NH3 started
10% NH3 started
Anhydrous NH3 started
% Decomposition
0
8
16
24
32
40
Time (min)
0
20
40
60
80
100
120
140
160

Figure 2

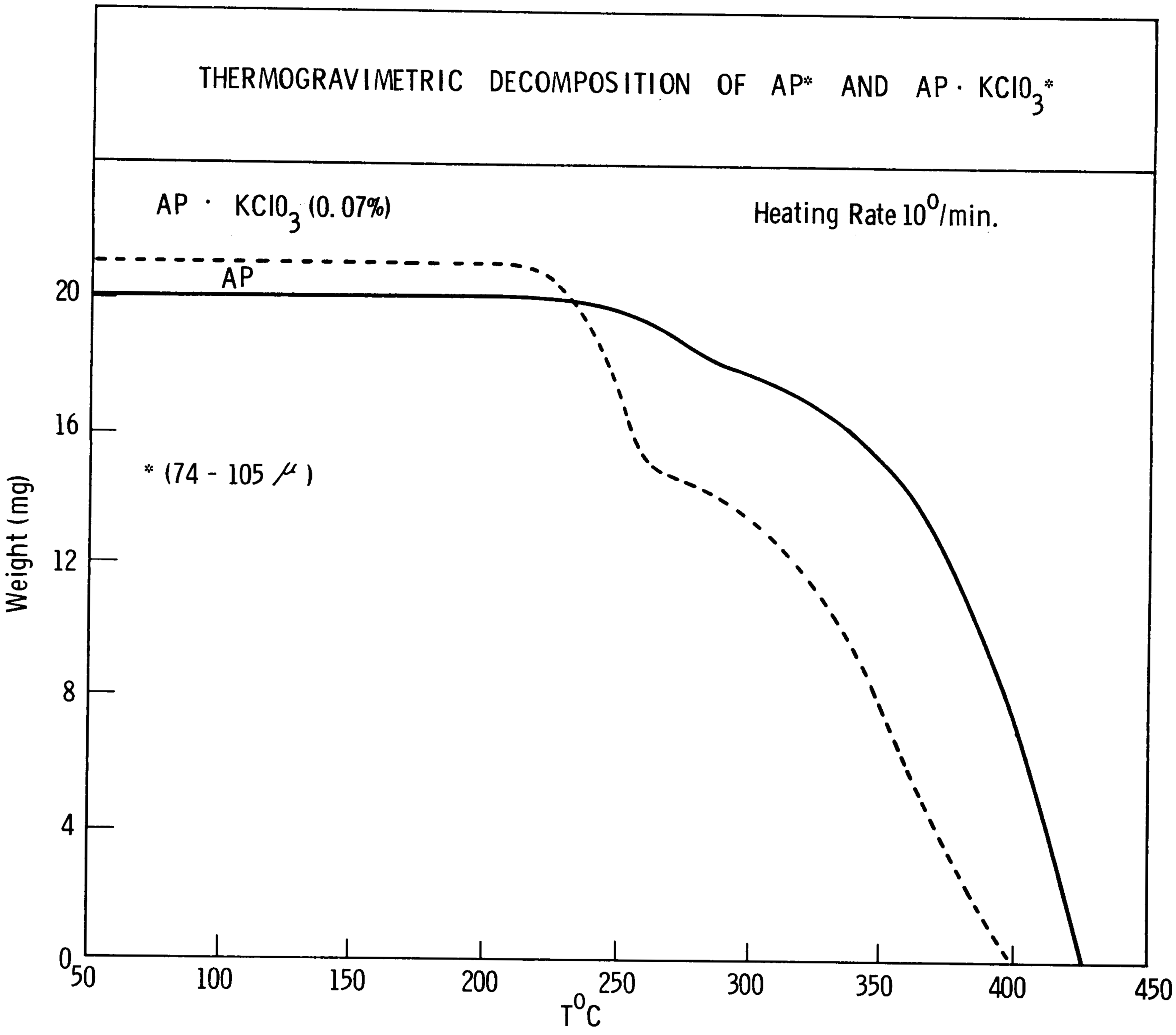
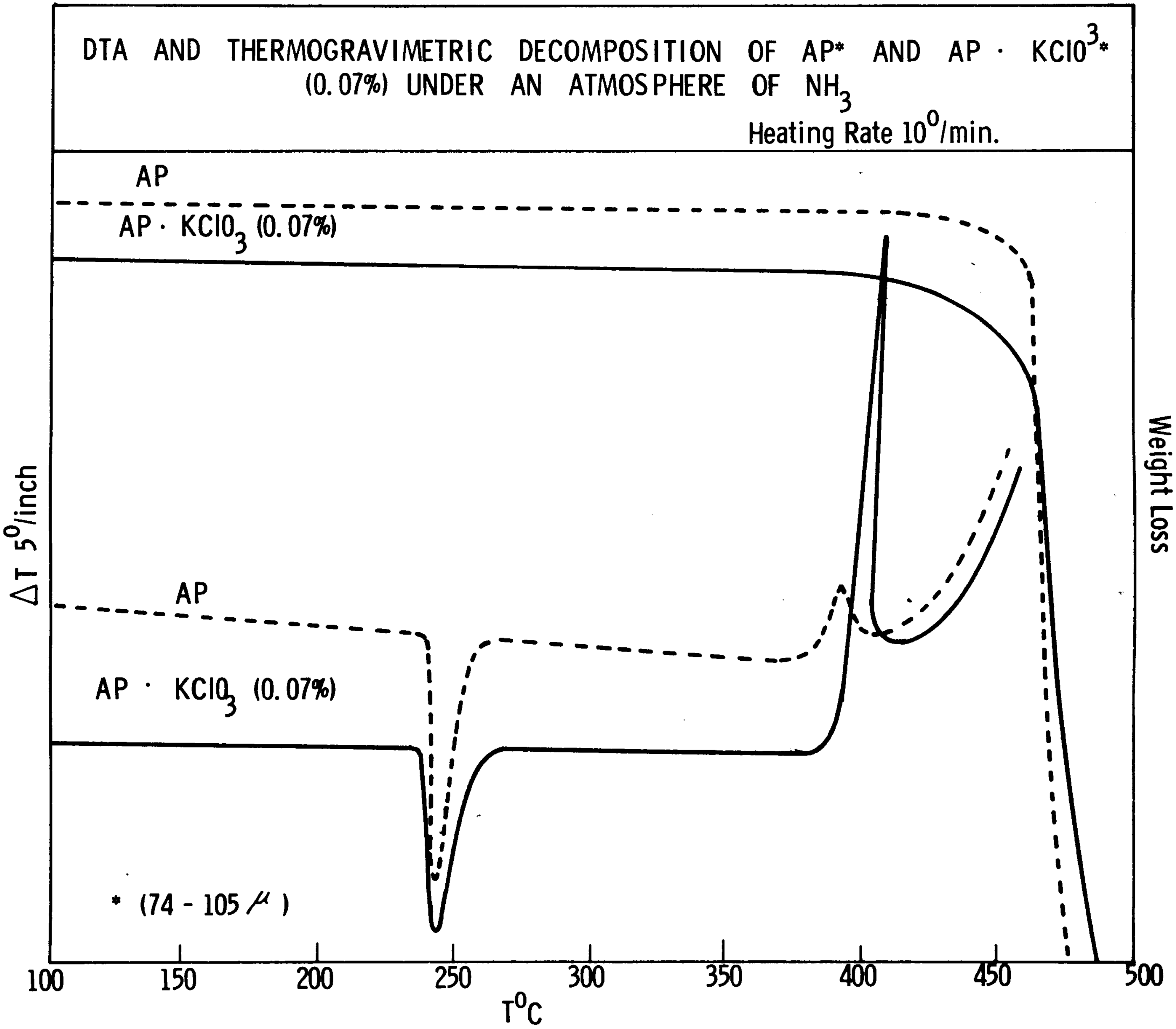

THERMOGRAVIMETRIC DECOMPOSITION OF AP* AND AP · $KClO_3$*
AP · $KClO_3$ (0.07%)
Heating Rate 10°/min.
AP
* (74 - 105 μ)
Weight (mg)
20
16
12
8
4
0
50
100
150
200
250
300
350
400
450
T°C

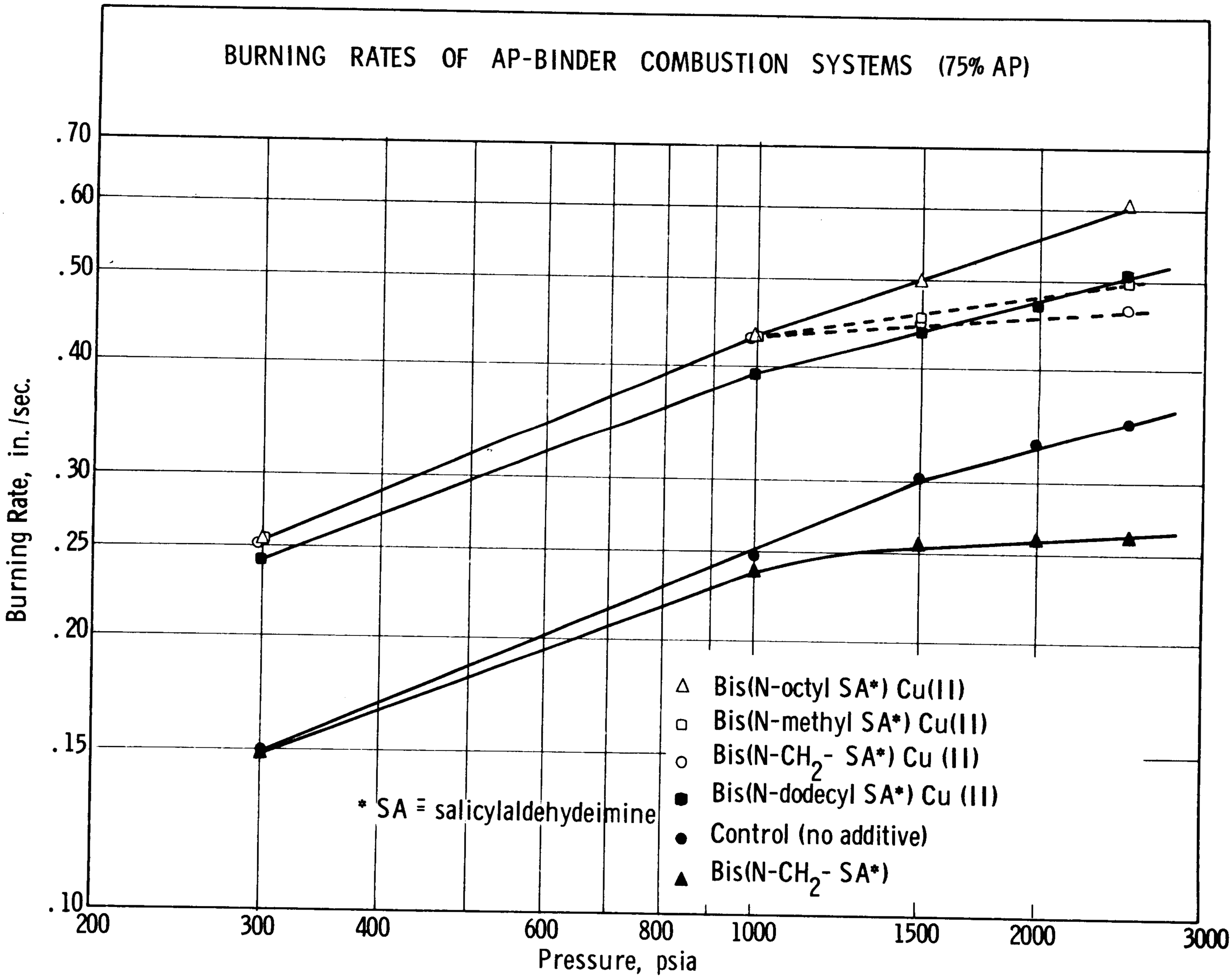
Figure 3



DTA AND THERMOGRAVIMETRIC DECOMPOSITION OF AP* AND AP · $KClO^3$* (0.07%) UNDER AN ATMOSPHERE OF NH_3

Heating Rate 10^0/min.

Figure 4



BURNING RATES OF AP-BINDER COMBUSTION SYSTEMS (75% AP)

Figure 5

DTA OF AP (74 - 105μ) WITH $CuCl_2 \cdot TEA$ (I)

Heating Rate 20°/min

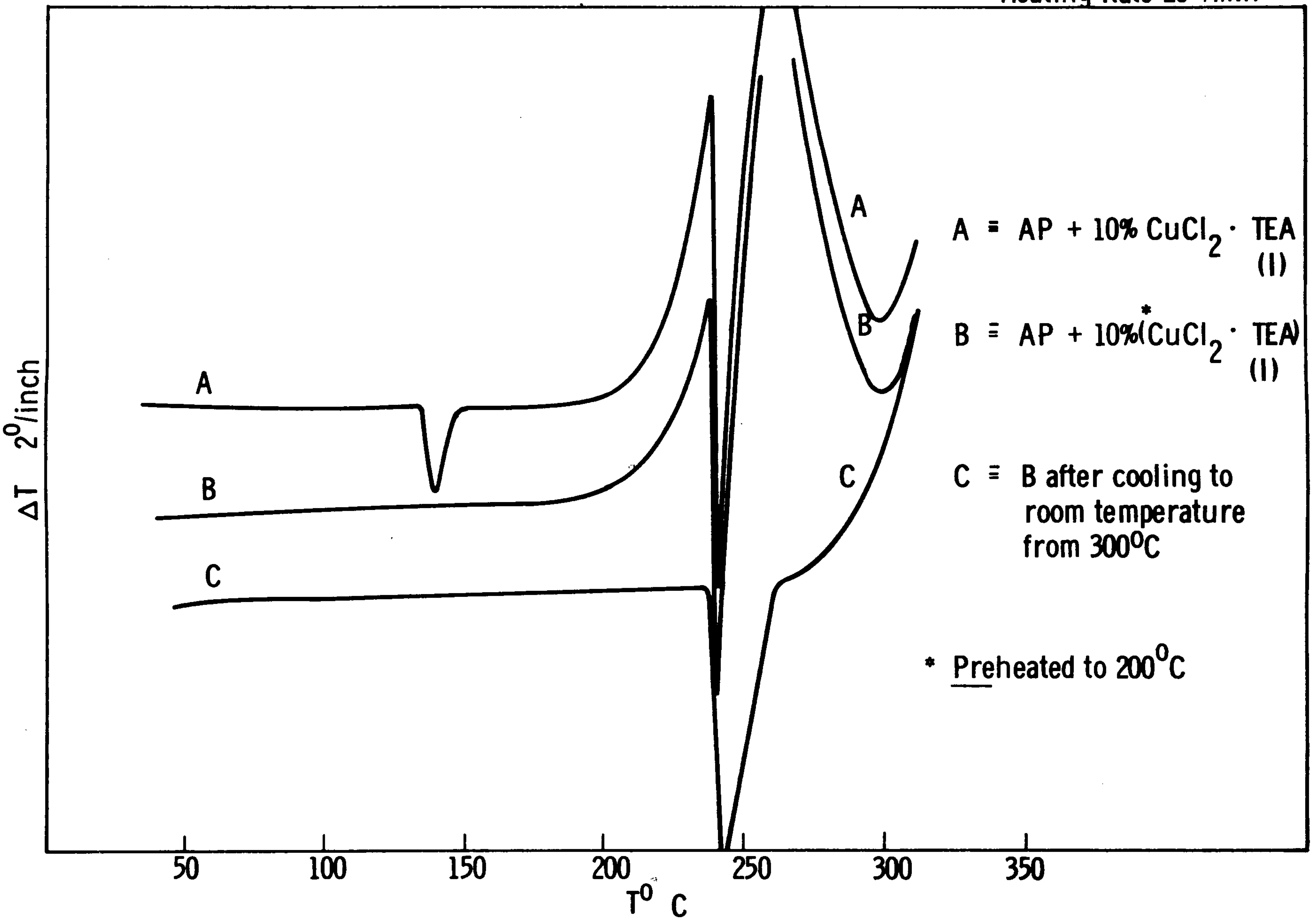


Figure 6

DTA of AP (TRIMODAL BLEND) WITH METALLOCENE ADDITIVES
(Constant Percent Iron)

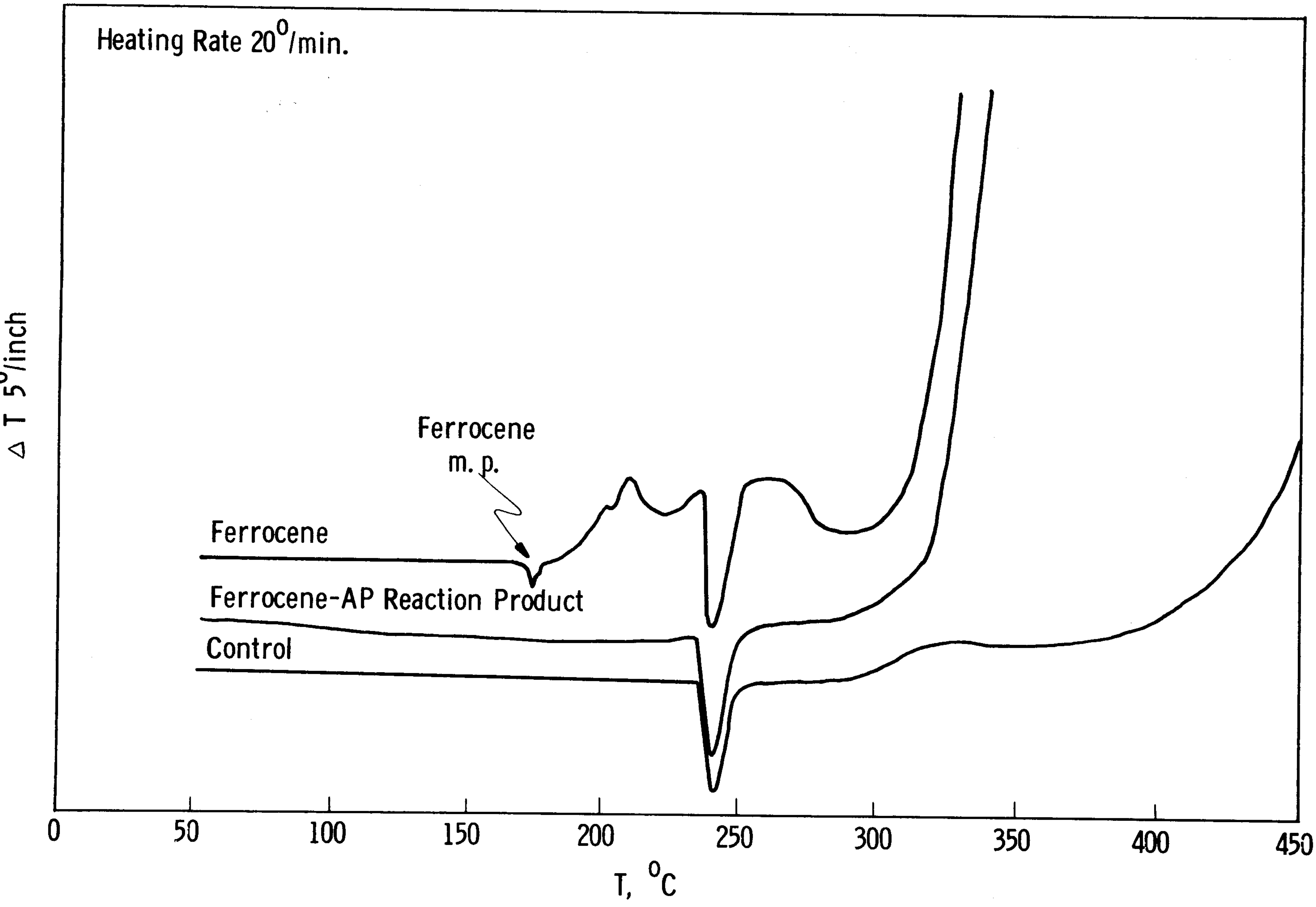


Figure 7

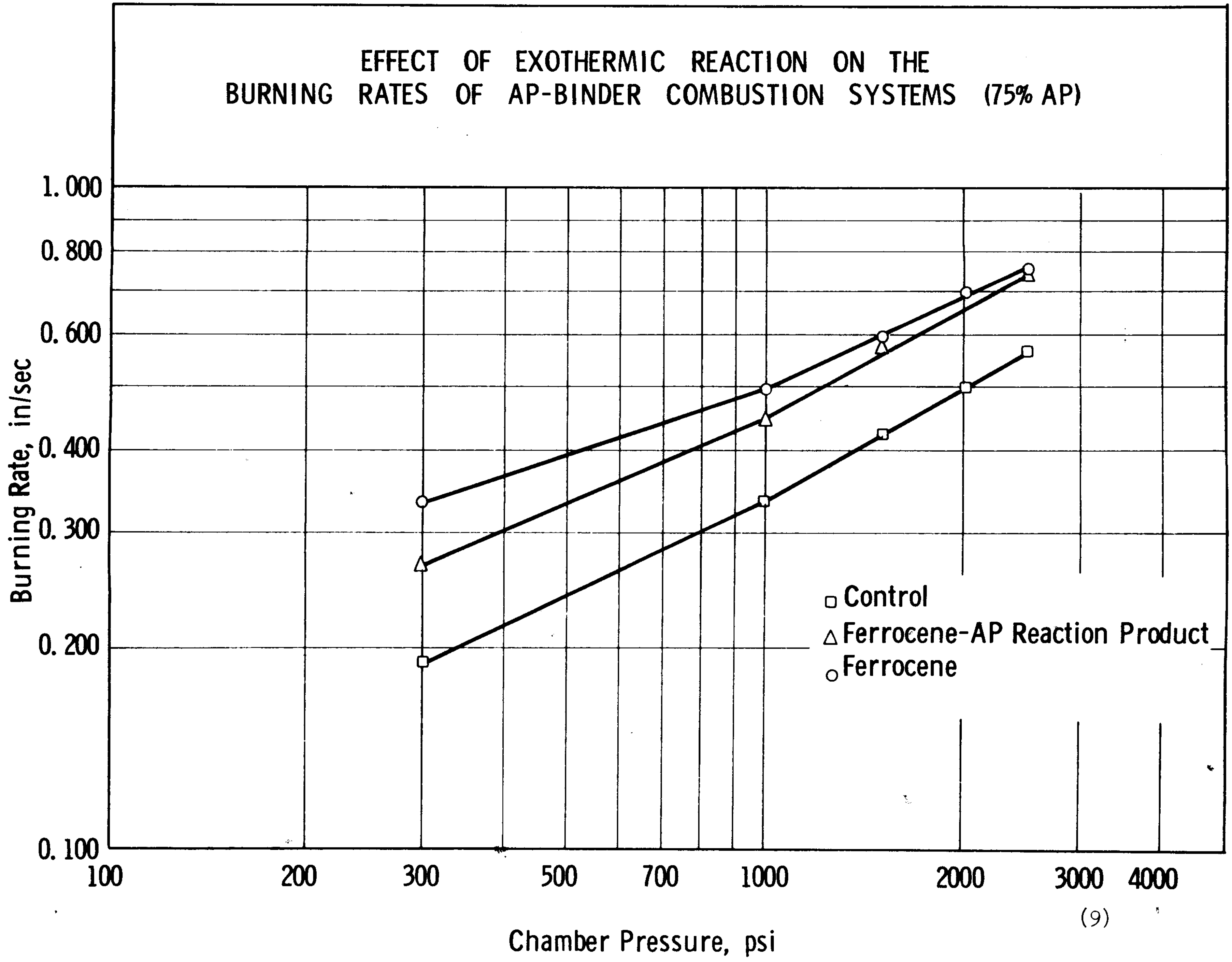

EFFECT OF EXOTHERMIC REACTION ON THE BURNING RATES OF AP-BINDER COMBUSTION SYSTEMS (75% AP)

Figure 8

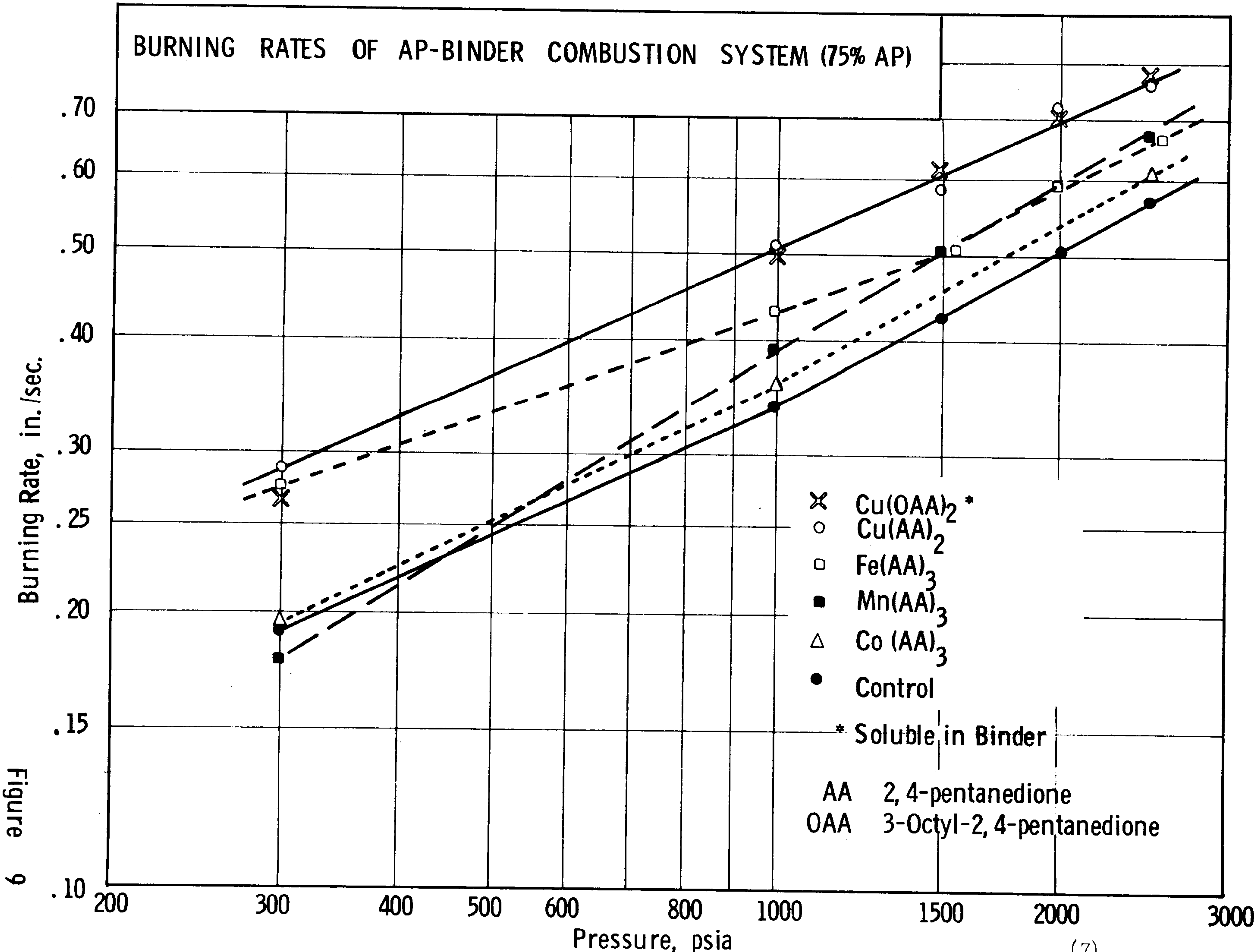
BURNING RATES OF AP-BINDER COMBUSTION SYSTEM (75% AP)
Burning Rate, in./sec.
.70
.60
.50
.40
.30
.25
.20
.15
.10
200
300
400
500
600
800
1000
1500
2000
3000
Pressure, psia
✕ Cu(OAA)2 *
○ Cu(AA)2
□ Fe(AA)3
■ Mn(AA)3
△ Co (AA)3
● Control
* Soluble in Binder
AA 2, 4-pentanedione
OAA 3-Octyl-2, 4-pentanedione

Figure 9

DTA AND THERMOGRAVIMETRIC DECOMPOSITION OF AP + 2.5% COPPER CHROMITE UNDER N_2 AND UNDER NH_3

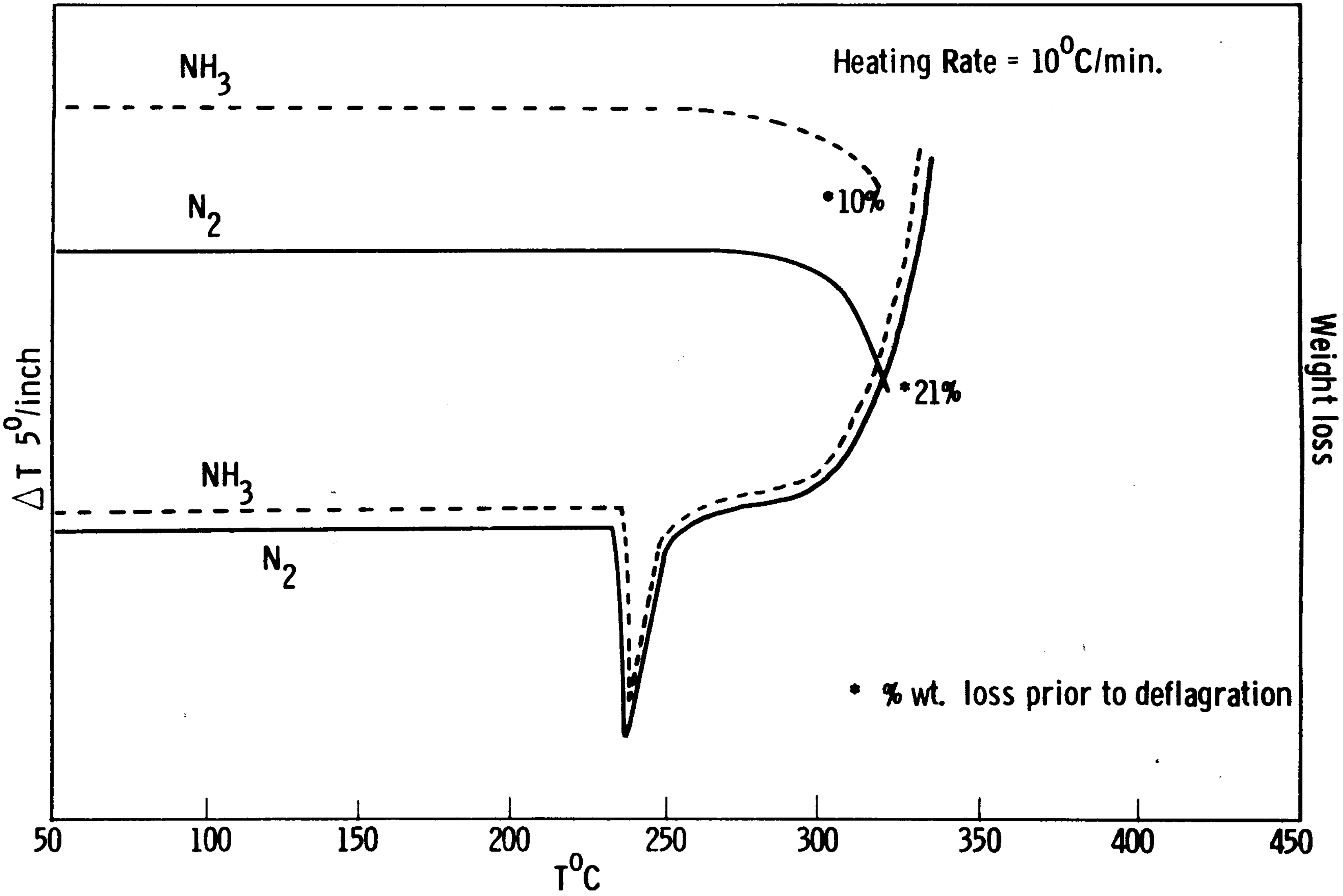


Figure 10

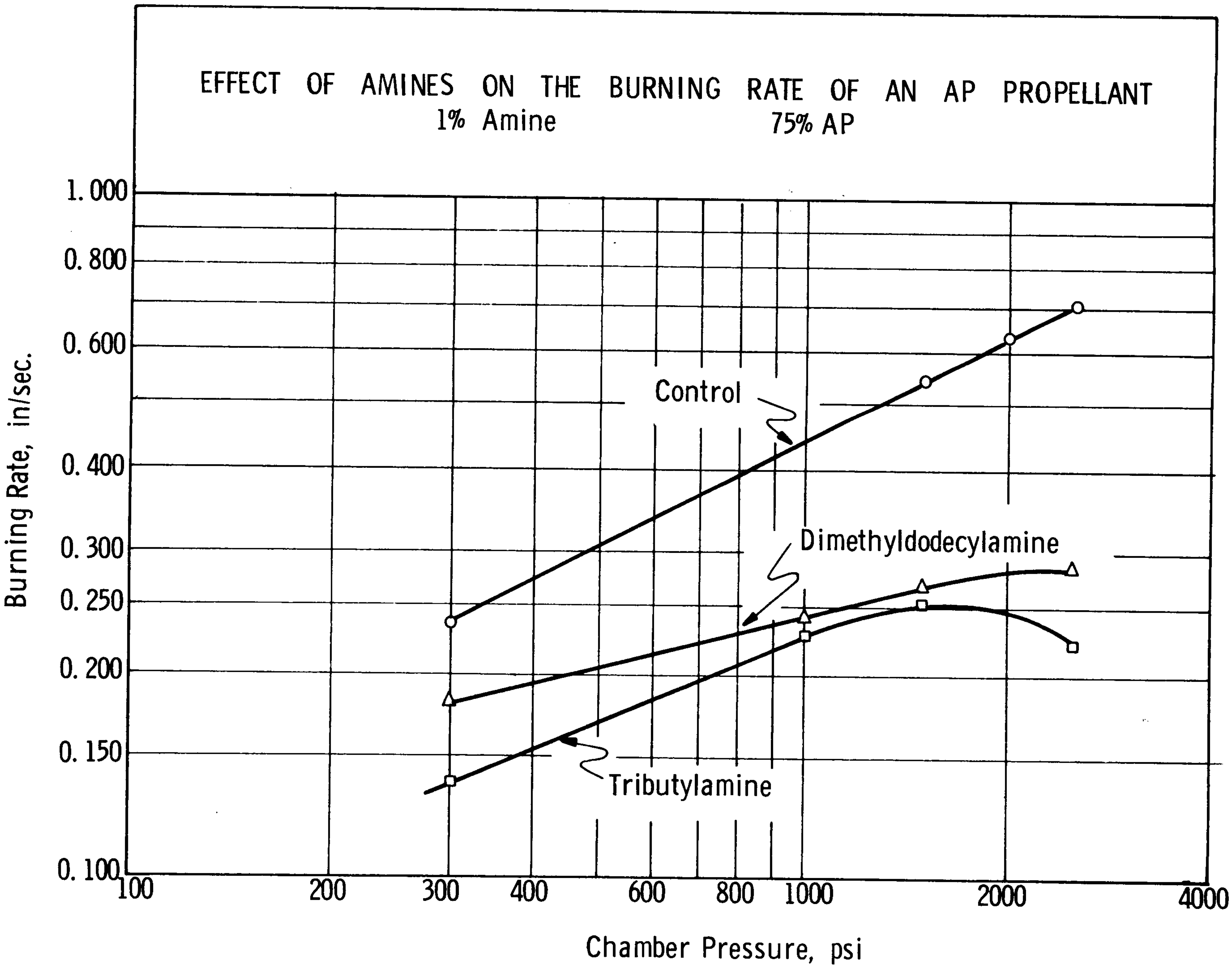

EFFECT OF AMINES ON THE BURNING RATE OF AN AP PROPELLANT
1% Amine
75% AP
Burning Rate, in/sec.
1.000
0.800
0.600
0.400
0.300
0.250
0.200
0.150
0.100
100
200
300
400
600
800
1000
2000
4000
Chamber Pressure, psi
Control
Dimethyldodecylamine
Tributylamine

Figure 11

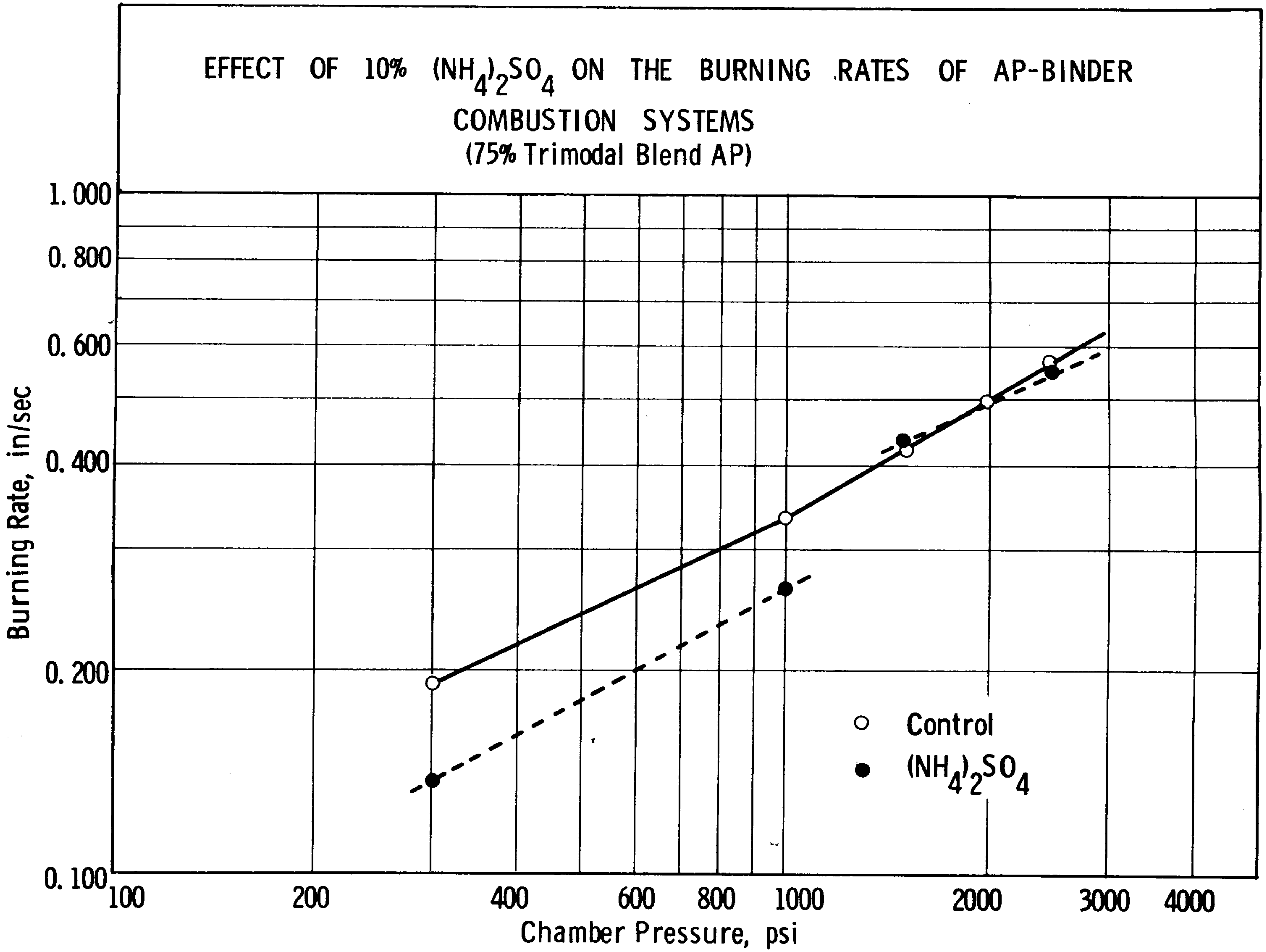

EFFECT OF 10% $(NH_4)_2SO_4$ ON THE BURNING RATES OF AP-BINDER COMBUSTION SYSTEMS
(75% Trimodal Blend AP)
1.000
0.800
0.600
0.400
0.200
0.100
Burning Rate, in/sec
100
200
400
600
800
1000
2000
3000
4000
Chamber Pressure, psi
○ Control
● $(NH_4)_2SO_4$

Figure 12

EFFECT OF PRESSURE ON AMMONIUM PERCHLORATE DECOMPOSITION
(Trimodal Blend)

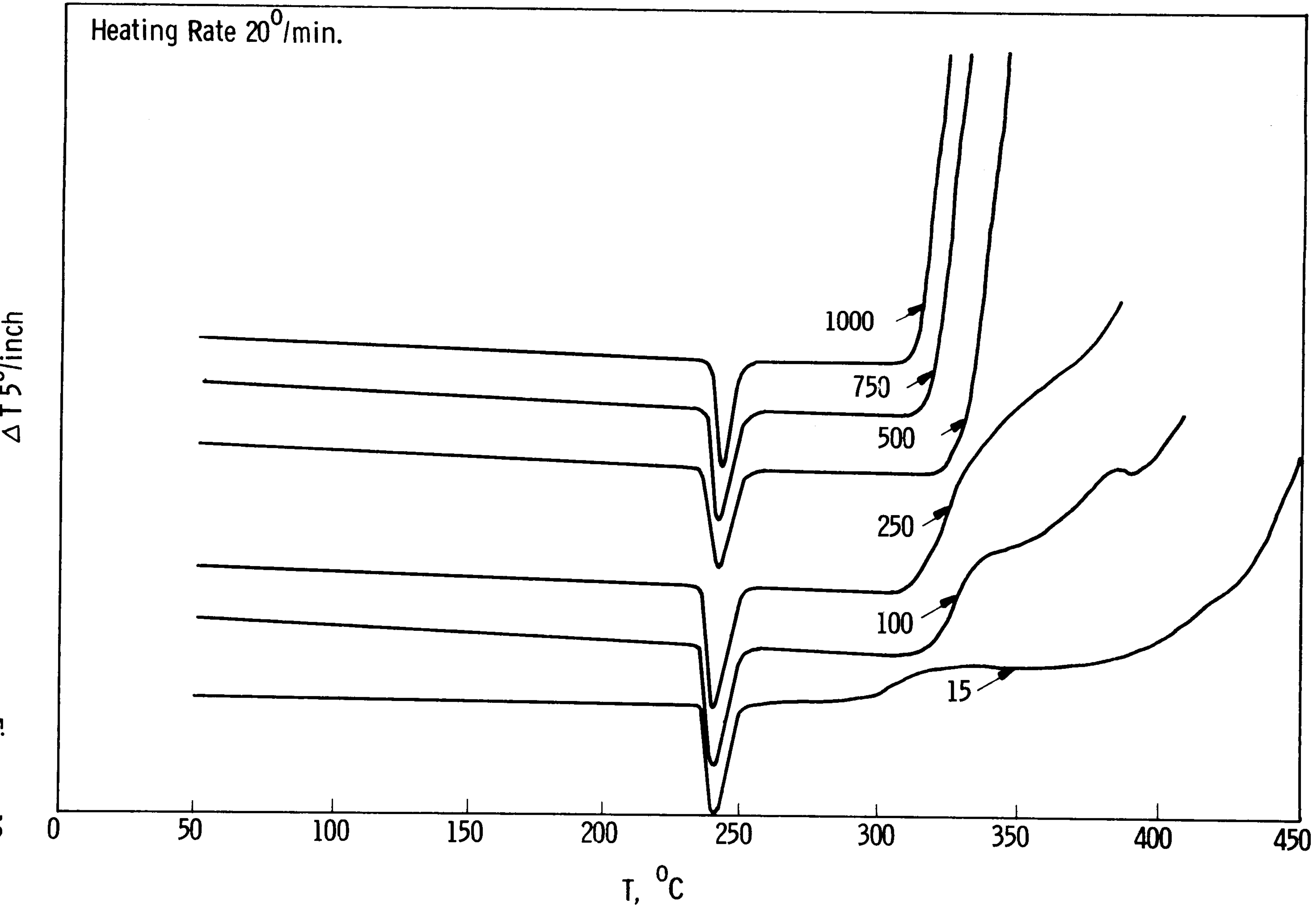
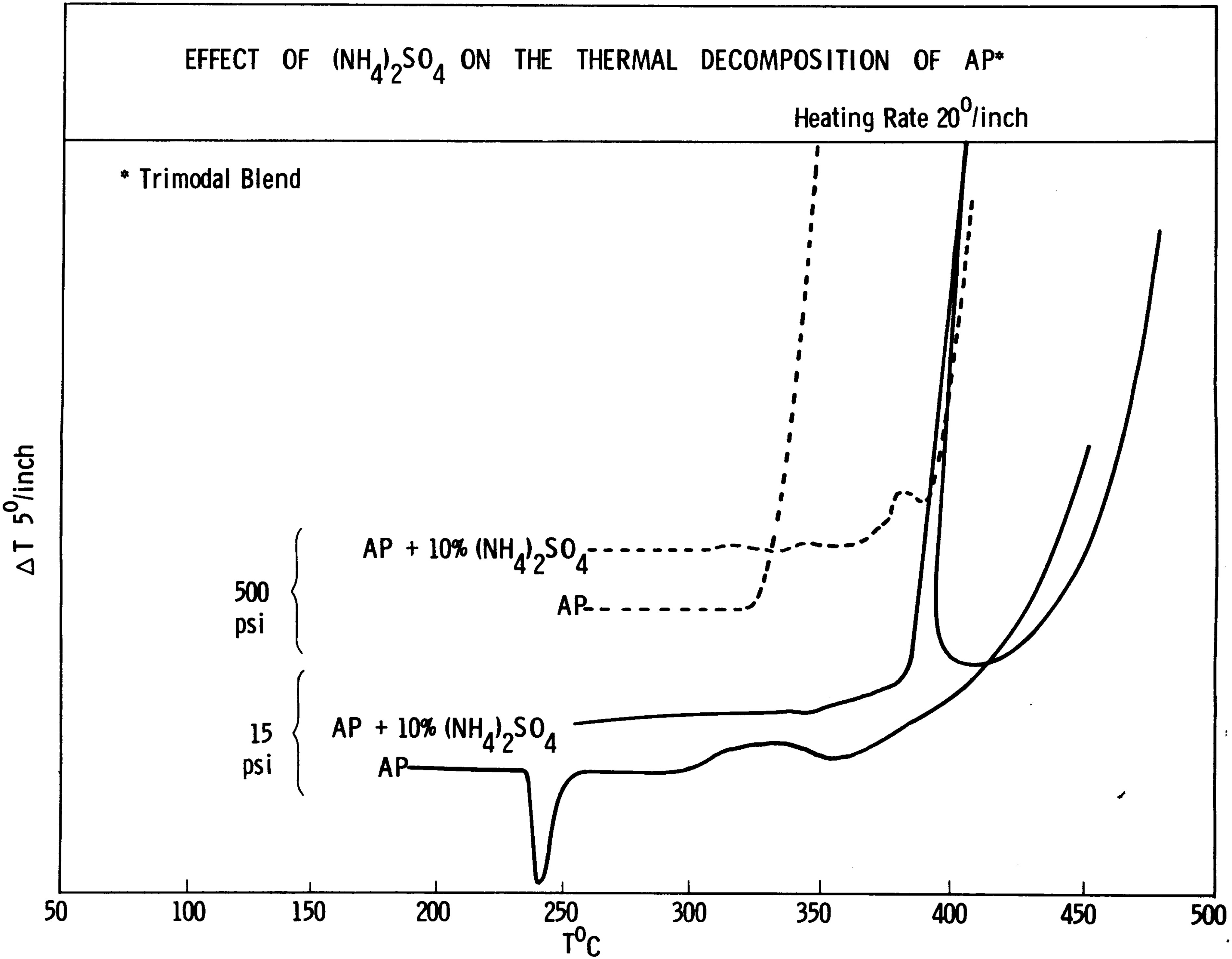


Figure 13



EFFECT OF $(NH_4)_2SO_4$ ON THE THERMAL DECOMPOSITION OF AP*

Heating Rate 20°/inch

Figure 14